I. REACTIONS OF ARYLLITHIUM COMPOUNDS WITH DIARYL KETONES

II. CARBOCYCLIC RINGS CONTAINING *p*-PHENYLENE UNITS

BY

GEORGE PHILLIP SPERANZA

B.S., Southern Methodist University, 1948
M.S., University of Illinois, 1949

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1951

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I. REACTIONS OF ARYLLITHIUM COMPOUNDS AND DIARYL KETONES

Introduction

The chemistry of hindered triarylmethyl derivatives has not been developed extensively because synthesis of such compounds is difficult. Mesitoyl radicals, in which the normal carbonyl function is suppressed, undergo *ortho*-arylation with phenylmagnesium bromide (1). This investigation was undertaken to determine the reactions of hindered diaryl ketones with aryllithium compounds, which are known to exhibit a greater tendency than Grignard reagents to add to α,β-unsatuated carbonyl compounds in the 1,2-manner (2). Reaction of phenyllithium with dimesityl ketone, which cannot undergo arylation in an *ortho*-position, does not yield the triarylcarbinol (3).

Discussion Of Results

Experiments with phenyl-, mesityl-, and duryllithium have made possible the synthesis of a number of new carbinols containing one mesityl or duryl radical. The only example of the class previously reported is diphenylmesitylcarbinol, prepared in poor yield from mesitylmagnesium bromide and benzophenone (4). Duryl- and mesityllithium combine with benzophenone to yield, respectively, diphenylduryl- and diphenylmesitylcarbinol. Mesityllithium adds to 3,4-dimethoxybenzophenone and 2,2′,4,4′-tetramethylbenzophenone to give 3,4-dimethoxyphenylmesitylphenyl- and 2,2′,4,4′-tetramethyldiphenylmesitylcarbinol. The latter compound is the most hindered triarylcarbinol which has been prepared and is sensitive to weakly acidic and basic solutions. Likewise, phenyllithium reacts with 3,4-dimethoxyphenylmesityl ketone and 2-methoxy-5-methylphenylmesityl ketone in the 1,2-manner (5). This type of behavior proved not to be general, however. Duryl phenyl ketone, duryl 4-methoxyphenyl ketone

and mesityl 3-methoxyphenyl ketone were arylated in the *ortho*-position by aryllithium compounds.

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II. CARBOCYCLIC COMPOUNDS CONTAINING *p*-PHENYLENE UNITS

Introduction

The application of the acyloin reaction to the preparation of bridged aromatic compounds has not been investigated. The relative ease by which macrocyclic acyloins may be prepared by the reaction of the diester and sodium indicated that intramolecular condensations of this type may be the preferred route to large carbocyclic ring compounds containing *p*-phenylene units. Experimentally, it has been found that eight methylene groups are required to join the two oxygen atoms in hydroquinone (1). A chain of six methylene substituents can link the meta positions of a benzene nucleus (2). It has been reported that one of the products of the polymerization of *p*-xylene is a cyclic compound containing two phenyl rings joined in the *para*-position by an ethylene chain (3). It was the purpose of this research to prepare and investigate

symmetrically substituted *p,p'*-diphenylalkane derivatives and examine their susceptibility to ring closure.

Discussion Of Results

Di-*para*-substitution of symmetrical diphenylalkanes was achieved by the Friedel-Crafts reaction. The reaction of bibenzyl and β-carbethoxypropionyl chloride yielded the desired product, *sym*-di-(*p*-carbethoxypropiophenyl) ethane. Similarly, ω-carbethoxyvaleroyl chloride and ω-carbethoxypelargonyl chloride gave the corresponding *p,p'*-bibenzyl derivatives. Reduction of the carbonyl groups resulted in the desired long chain dibasic esters containing two *para*-phenyl groups. When *sym*-di-(*p*-carbethoxytrimethylenephenyl) ethane was allowed to react with sodium the acyloin resulting from intramolecular cyclization was obtained in a 58 per cent yield. The structure was verified by an examination of the infrared absorption spectrum, preparation of the 2,4-dinitrophenylosazone, 2,4-dinitrophenylhydrazone, molecular weight determination and by the analytical data. Evidence that cyclic acyloins are obtained from *sym*-di-(*p*-carbethoxypentamethylenephenyl) ethane and *sym*-di-(*p*-carbethoxynonamethylenephenyl) ethane is substantiated by the infrared spectrum, analyatical data and by the preparation of a 2,4-dinitrophenylosazone.

Another investigation was undertaken to determine whether ring closure could be achieved by the coupling action of the binary mixture of magnesium and iodine. This reagent is specific for coupling diaryl ketones and with benzophenone a quantitative yield of benzopinacol is obtained (4). The five compounds studied were *sym-p,p'*-dibenzoyl derivatives of bibenzyl, 1,4-diphenylbutane, 1,6-diphenylhexane, 1,6-diphenoxyhexane and 1,10-diphenyldecane. A variety of conditions were used in attempting cyclization, but in no instance could any of the desired material be obtained. Starting material was recovered in every experiment.

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VITA

The author was born on August 27, 1924, in Johnston City, Illinois, where he received his elementary education. He was inducted into the Army of the United States in March, 1943. On June 4, 1944, he was married to Phylis Jane Scoles. Upon discharge from the Army in 1945, he entered Southern Methodist University and received the degree of Bachelor of Science from that institution in June, 1948. He entered the Graduate College of the University of Illinois in the summer of 1948. From this University he received the Master of Science degree in June, 1949.

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